

catalyst appeared to remain active for THFDM production when HMF was reduced first to FDM with the Co catalyst. HMF feed concentrations of 1%, 3%, and 6%, were tested, all giving similar conversions and selectivities.

Additional experiments were conducted utilizing the staged Co/Ni catalysts at high temperatures with either HMF or FDM feeds to examine polyol production (FIGS. 62-70). Temperatures as high as 180° C. were evaluated. The major product was 1,2,6-hexanetriol but yields decreased with increased temperatures with production of may unknown products. One major by-product was identified as 2,5-hexanediol. When the feed was THFDM however, almost no ring-opening occurred. THFDM was quite stable up to 200° C. Ring-opened polyols therefore likely are formed via HMF or FDM, not via THFDM. FIGS. 62-70 show the results obtained under a variety of temperatures, feed (FDM vs. HMF) feed concentration and space velocity.

A batch-wise experiment was conducted to study the effect of organic solvent on the catalytic hydrogenation of HMF to FDM utilizing two different catalysts. Selectivity toward FDM production was compared for reactions conducted in ethanol and reactions conducted in water. As shown in Table 7, conversion and selectivity toward FDM are lower in ethanol than in water under the same reaction conditions and reaction times.

TABLE 7

Effect of Organic Solvent on HMF Reduction							
		60° C. 500 psi H ₂			100° C. 950 psi H ₂		
		Time	Conversion	Selectivity	Time	Conversion	Selectivity
Co/SiO ₂	H ₂ O	4 hr	100%	96%	1 hr	98%	83%
	EtOH	4 hr	1%	16%	1 hr	2%	49%
Pt/Al ₂ O ₃	H ₂ O	2 hr	94%	98%	1 hr	89%	96%
	EtOH	2 hr	82%	98%	1 hr	53%	96%

The impact of various impurities on the hydrogenation of HMF was investigated in both batch-wise and flow reactor studies. Impurities included fructose, ethyl acetate, dimethylacetamide, methyl t-butyl ether, methyl iso-butyl ketone, levulinic acid, formic acid, acetic acid, sodium sulfate, and N-methyl pyrrolidinone. These impurities were found to be non-detrimental to HMF conversion within the accuracy of the experiments.

Of particular interest were the results with fructose impurity in batch experiments conducted between 60 and 100° C. and 500 psi for at least 2 h. Both Pt(Ge)/C (Engelhard #43932) and Co/SiO₂ (Sud Chemie G62aRS) catalysts converted HMF to reduced products without reducing fructose to sorbitol or mannitol, even at high HMF conversions. FDM can be formed in high yield. In the absence of HMF, fructose is easily reduced under these reaction conditions, suggesting that HMF either inhibits fructose reduction or is reduced at a faster rate. These results indicate that highly selective reduction of HMF is possible with the HMF precursor fructose present in the feed and that fructose need not be separated from the HMF solution prior to reduction.

Example 5

Reduction of HMF in the Presence of Fructose

Batch-wise experiments were conducted with an aqueous solution of 15 wt % each of HMF and fructose under 500 psi

H₂ between 75 and 100° C. using Ge-promoted 5% Pt on carbon (Engelhard #43932) for at least 2 h. In a sample taken at 1 h, LC and ¹³C NMR analysis showed that HMF was converted to FDM with good selectivity but that essentially no fructose was converted to sorbitol or mannitol even at high HMF conversion. Only trace amounts of levulinic and formic acids were formed.

FIGS. 71-80 show the results of a number of batchwise HMF conversion reactions utilizing RANEY® Co-2724 (FIG. 71); 5% Pt(Ge)/C (FIG. 72); 5% Pd/C (FIG. 73); 5% Ru/C (FIG. 74); RANEY® Co-2700 (FIGS. 75-76); and RANEY® Cu (FIG. 77) catalysts. The effect of H₂ pressure was investigated utilizing a 5% Pt(Ge)/C catalyst as shown in FIG. 78. FIG. 79 shows the effect of temperature on HMF conversion using the Pt(Ge)/C catalyst, and FIG. 80 shows the effect of temperature on FDM selectivity for the Pt(Ge)/C catalyst.

Reaction methods of the invention for selective reduction of HMF to produce FDM and/or THF dimethanol have many advantages relative to conventional technologies. The reaction temperature of the inventive methodology is relatively low, thereby reducing unwanted side reactions and decomposition of reactants and/or products, and allowing increased selectivity. The hydrogen pressure is also low resulting in reduced operating costs. Since the solvent utilized is water

rather than an organic solvent, the methodology is relatively less expensive and more environmentally friendly than many conventional processes. The reaction rates obtained through the methodology of the invention are high, allowing highly efficient continuous flow reactors to be utilized.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

The invention claimed is:

1. A method of reducing hydroxymethylfurfural (HMF), comprising:
 - a) providing a starting material and a solvent into a reactor, the starting material comprising HMF and the solvent consisting of water;
 - b) providing H₂ into the reactor; and
 - c) contacting the starting material with a catalyst comprising at least one metal selected from Co, Ir, Re and Rh, the contacting being conducted at a reactor temperature of less than or equal to 250° C.
2. The method of claim 1 wherein the contacting is conducted at a reactor temperature of less than or equal to 180° C.